

Advanced Diagnostics of Layered-Oxide Particles

Principal Investigators: William Chueh, Mike Toney, Yi Cui,
SLAC National Accelerator Laboratory

Project ID: bat370

Overview

Timeline

- Start: Oct 1, 2017
- End: Sep 30, 2019
- Percent complete: 100%

Budget

- Funding for FY19
\$450k

Barriers

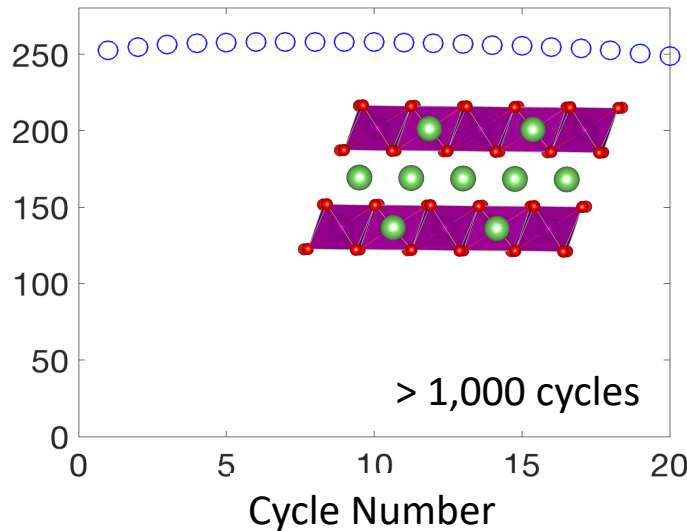
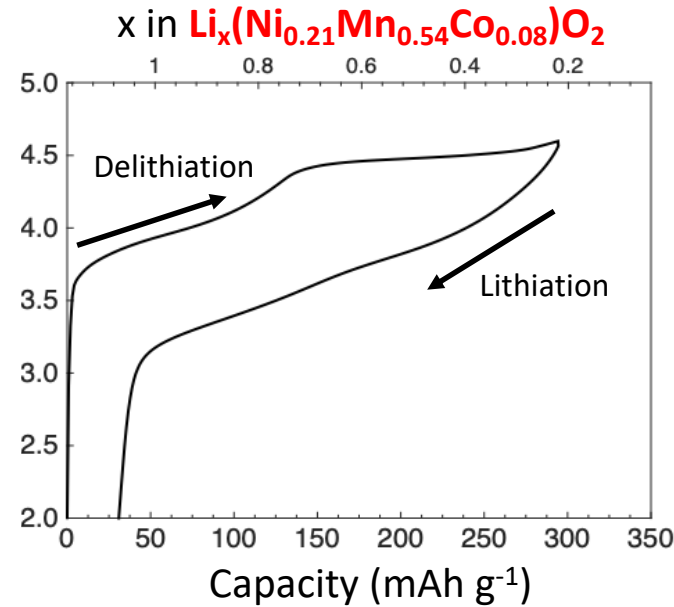
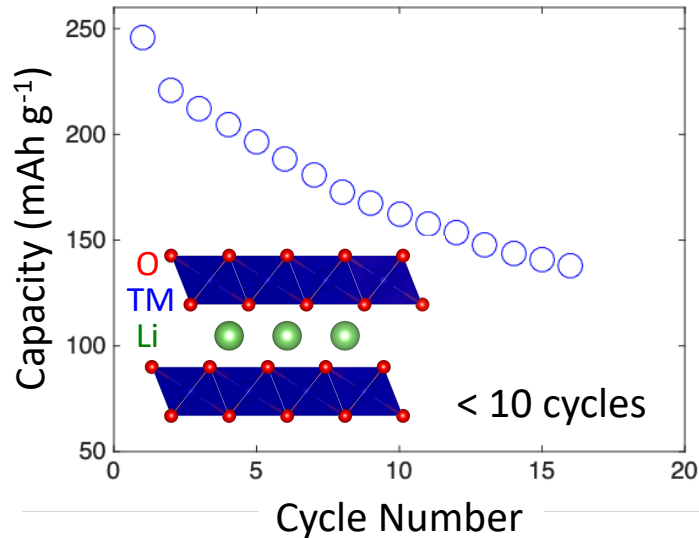
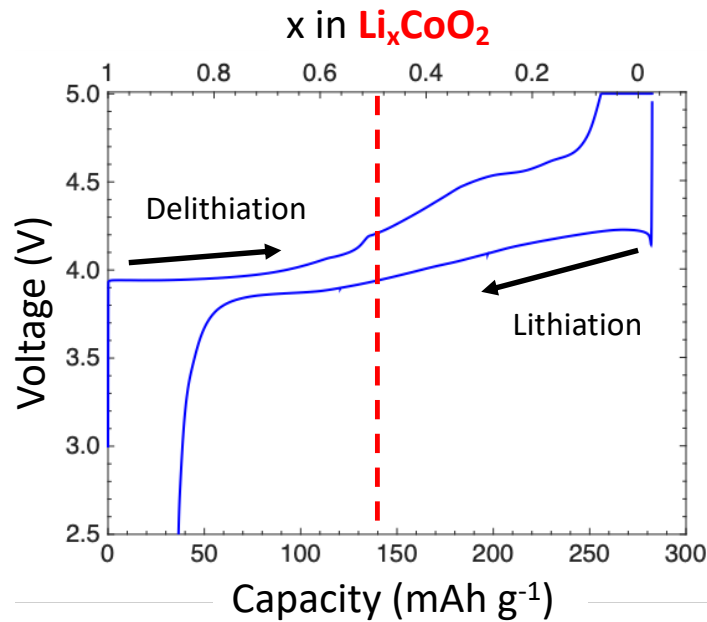
Barriers addressed

- Advanced in-situ diagnostic to pinpoint and predict failures in batteries
- Screen new battery chemistries using advanced diagnostic
- Electrode lifetime

Partners

- PIs: Yi Cui, Will Chueh, Mike Toney
- Collaborators:
 - Gerbrand Ceder (LBNL)
 - Wanli Yang (LBNL ALS)
 - David Prendergast (LBNL TMF)
 - Industry (materials)

Project Objective

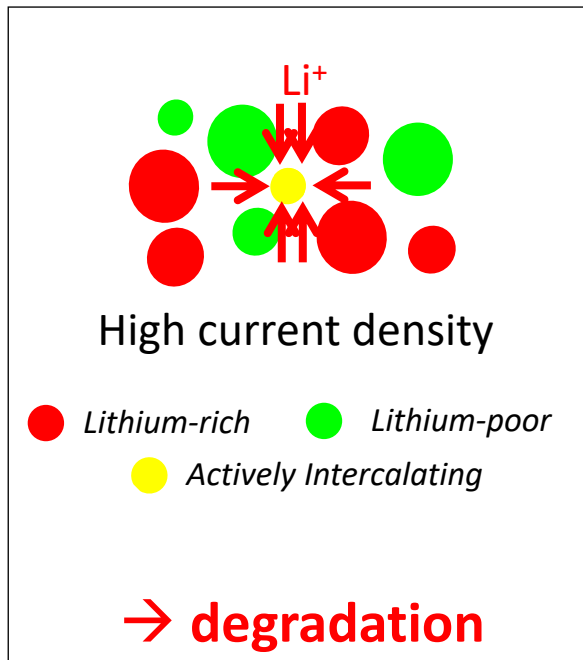


- In LCO, delithiating beyond half Li filling causes irreversible phase transition and fast capacity degradation.
- In LMR-NMC, however, delithiating to well beyond half Li filling gives excellent cycling performance, albeit this comes at the expense of large voltage hysteresis and voltage fade.
- **The objective of this work is to understand the origin of activation and degradation of LMR-NMC.**

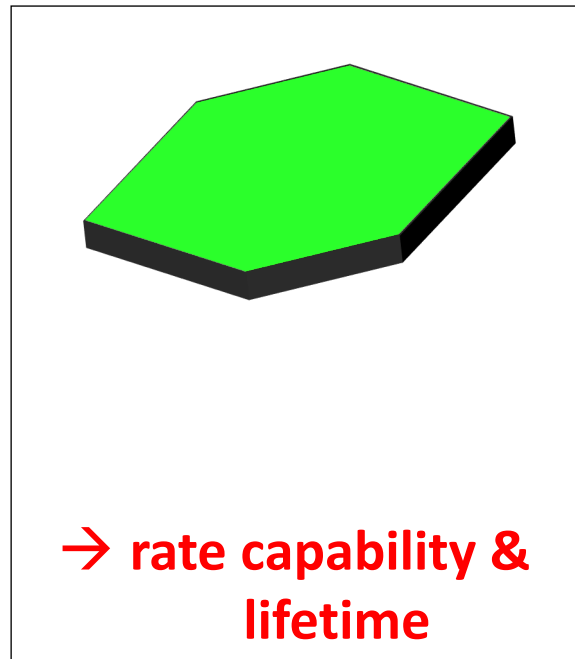
Project Objective

Objectives: Develop and utilize a correlative microscopy platform to investigate the (de)lithiation dynamics of LMR-NMC and NMC, with the specific goal of understanding factors that determine the rate capability and degradation mechanisms at the secondary particle, single primary particle, and atomistic length scale.

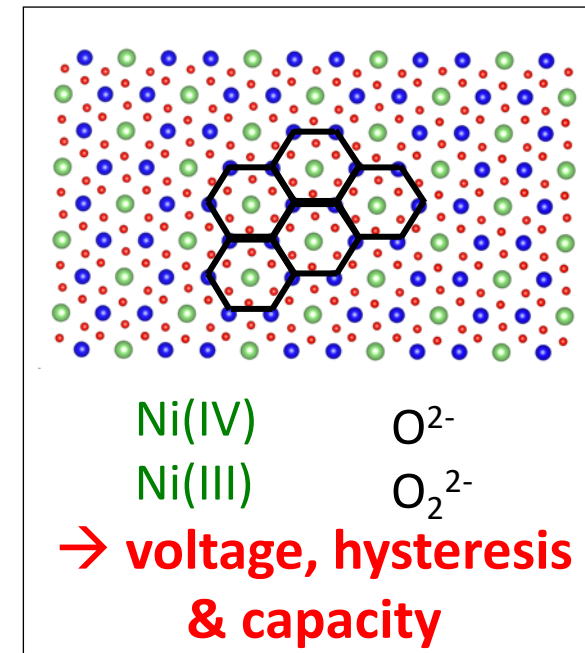
Macroscale: Hot Spots



*Mesoscale: Kinetics
& Chemo-mechanics*



Atomic: Redox



Relevance & Impact

Relevance:

- Understand atomistic and mesoscale factors that lead to capacity & voltage fading in layered oxide cathode (LMR-NMC & NMC)
- Develop diagnostic tools that reach new length scales not previously available

Impact:

- Enable accelerated materials development time by understanding capacity & voltage fade mechanisms
- Provide new information to design fast charging protocols and to improve power density

Milestones

FY 2018

- Use of correlative microscopy platform for imaging LMR-NMC and NMC cathode hotspots. (Achieve Q1 2018)
- Spectro-imaging of single NMC particles. (Achieved Q4 2018)

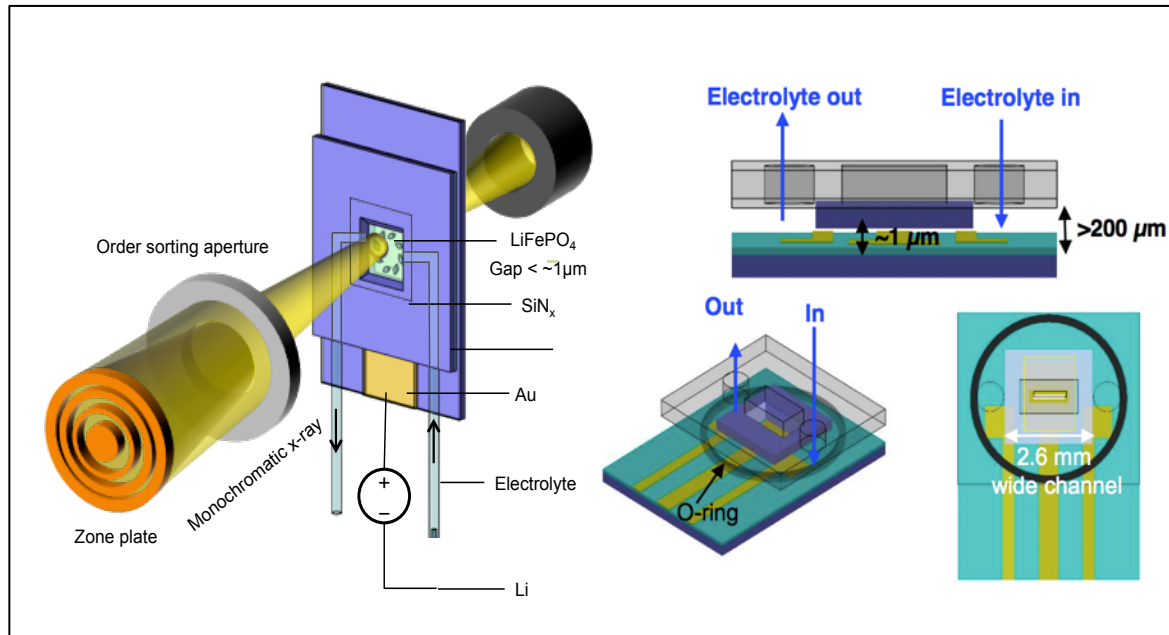
FY 2019

- Quantify the local structure of Li-rich layered oxides using local X-ray probe. (Achieved Q1 2019)
- Assess the effect of synthesis condition of anion redox. (Achieved Q4 2019)
- Assess the effect of oxygen vacancies on anion redox. (Achieved Q4 2019)

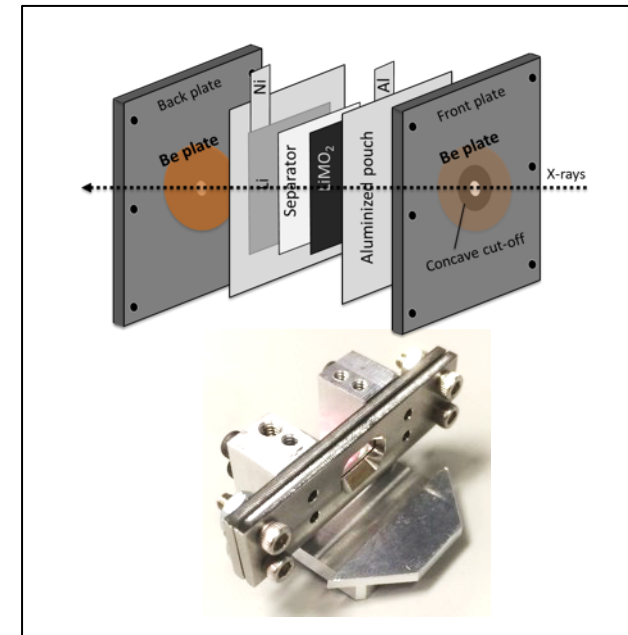
Approach

- Develop & utilize in-situ & ex-situ X-ray spectroscopy, diffraction and microscopy to relate local chemistry, structure and microstructure evolution to battery electrochemical characteristics (voltage, capacity/voltage fade, and activation)
- Correlate with other characterizations such as diffraction & electron microscopy.

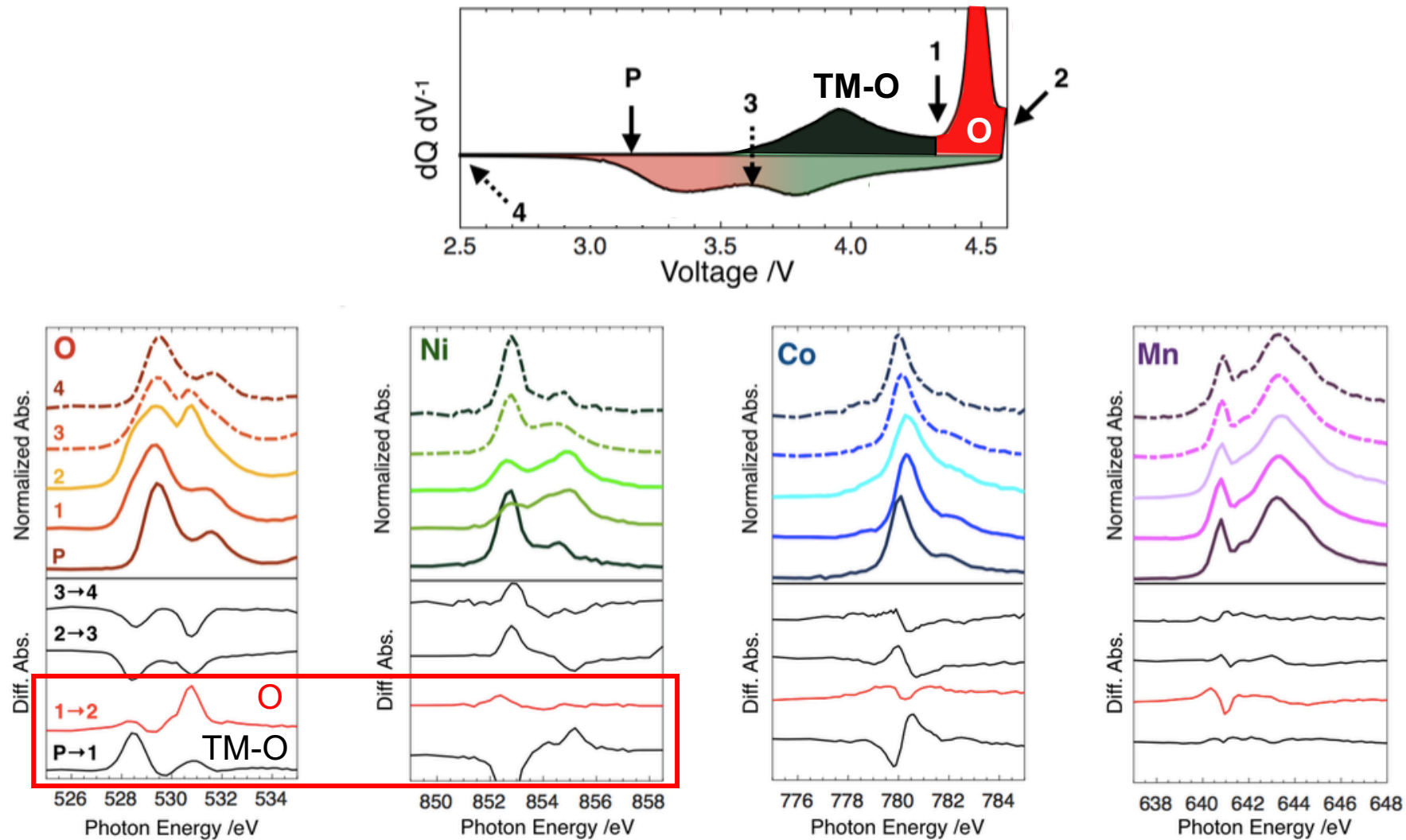
Soft X-ray Spectro-microscopy



Hard X-ray Diffraction, Spectroscopy & Microscopy



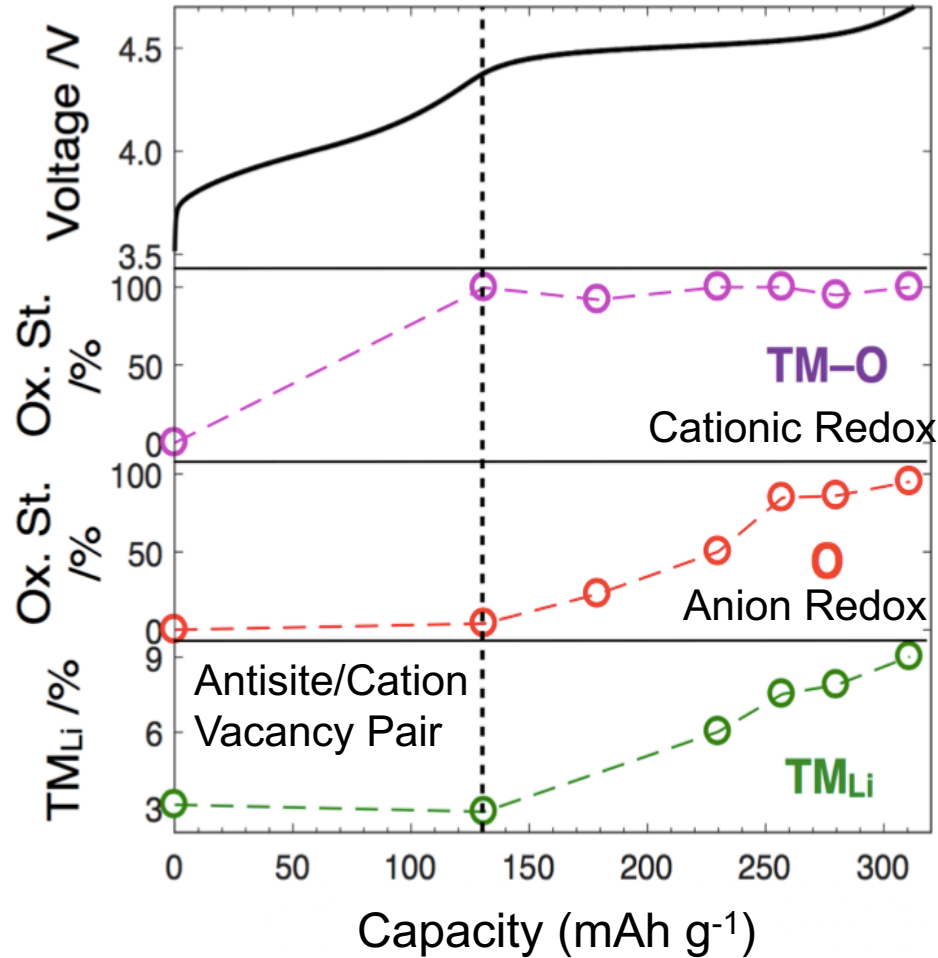
Technical Progress: What are the redox centers? Going beyond TMs



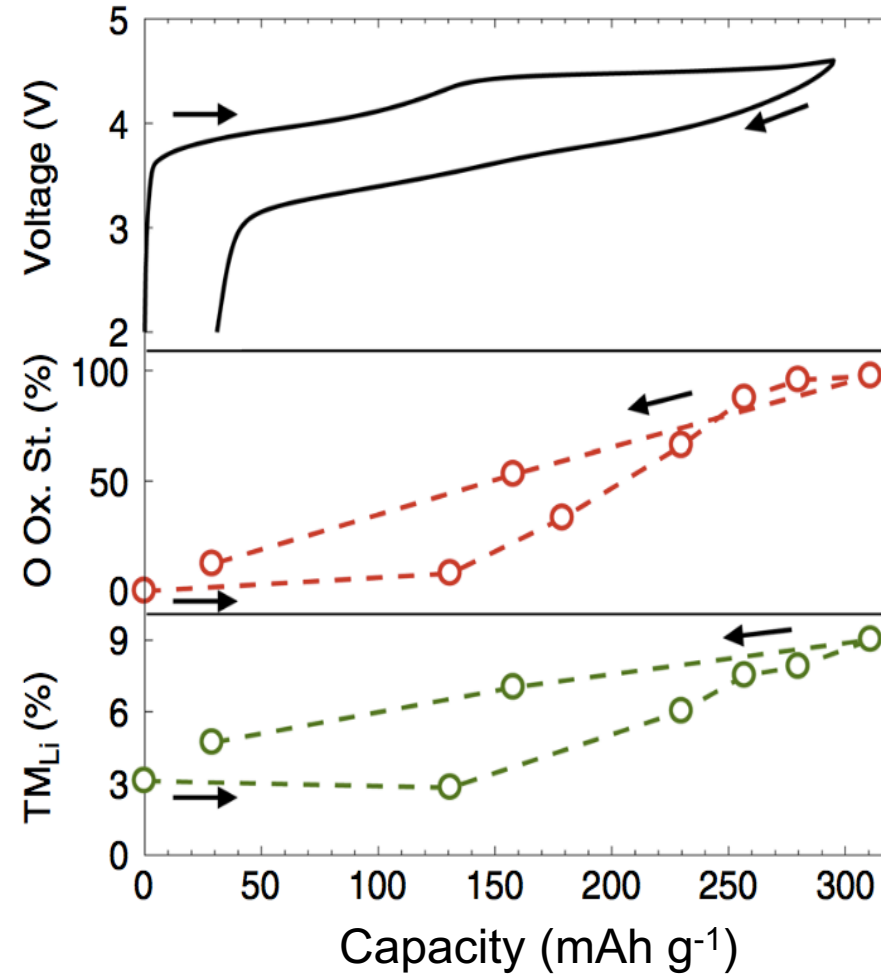
Through soft X-ray spectroscopy, we show that below 4.2V, redox partner upon delithiation is Ni-O (covalent); above 4.2V, the redox partner is essentially pure O (non-bonding).

Technical Progress: Coupling between cation migration & anion redox

Cation migration & *plateau*

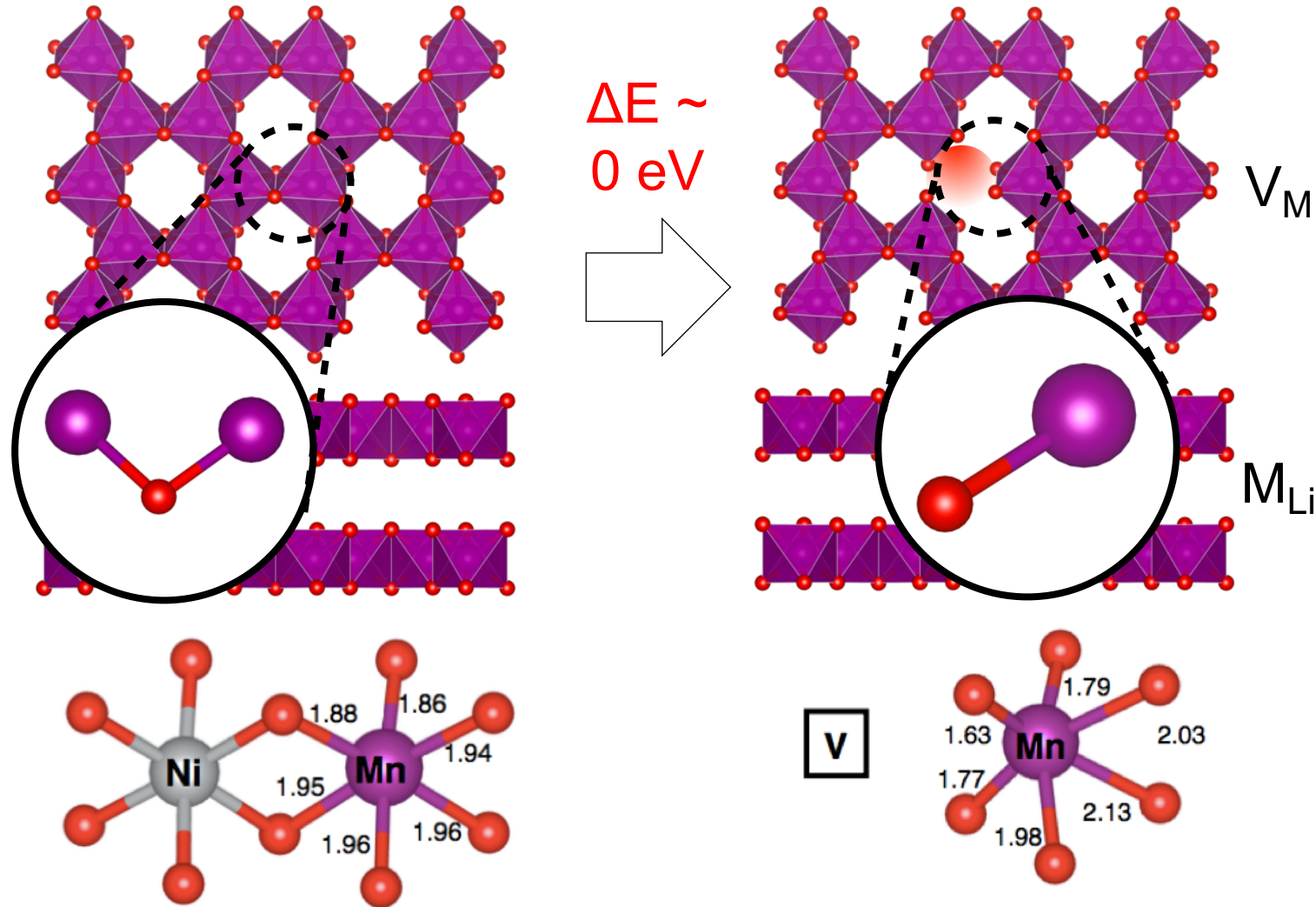


Cation migration & *hysteresis*



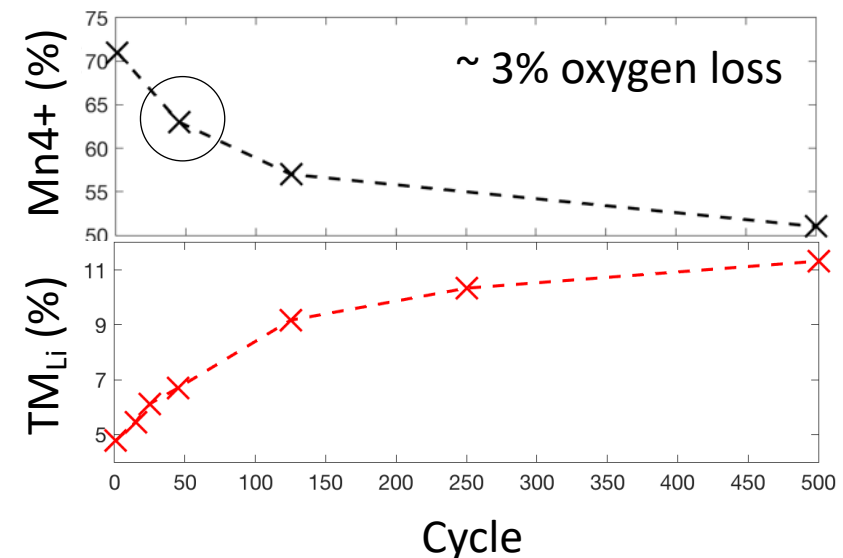
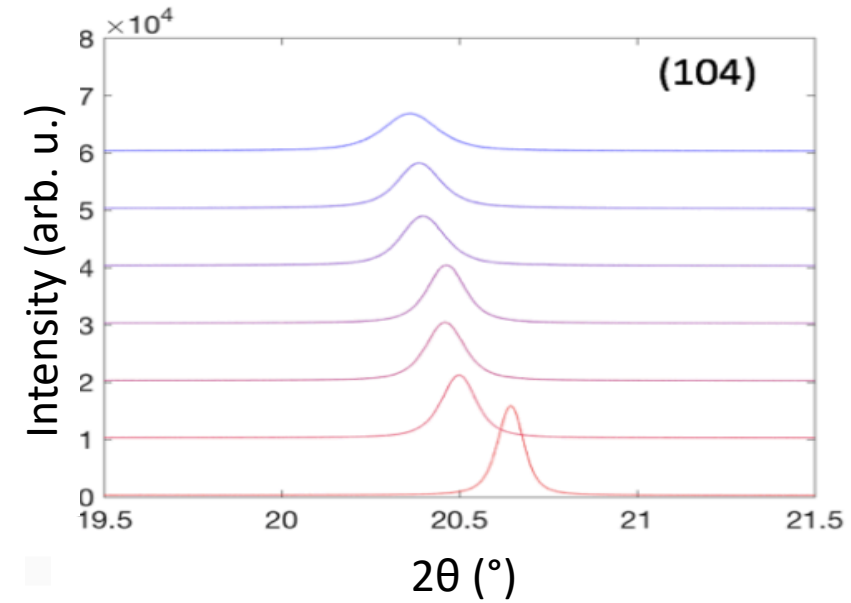
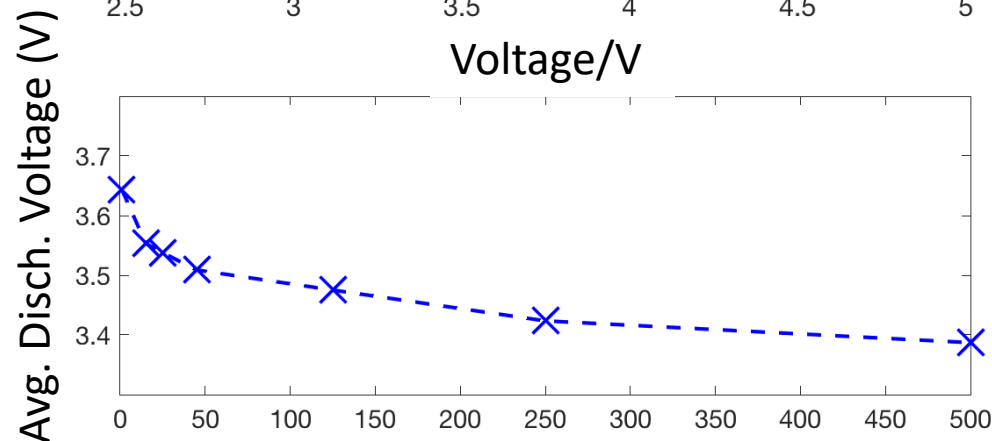
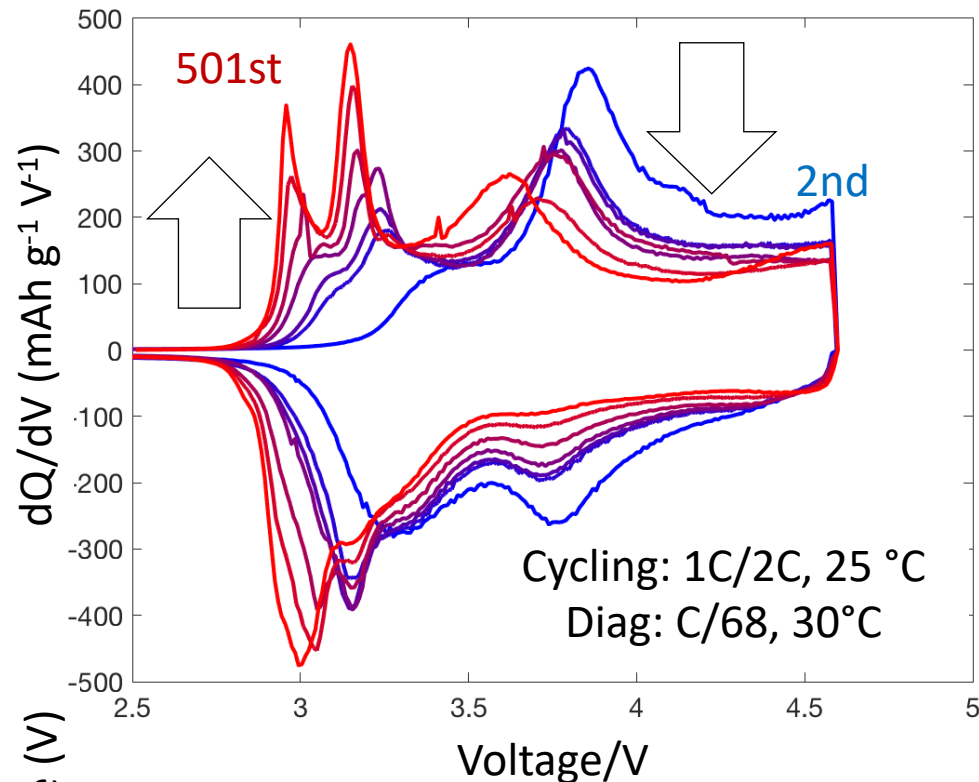
Above 4.2V, the oxygen redox capacity is accompanied by substantial cation migration (i.e., formation of antisite/cation vacancy pair). On discharge, the cations partially migrate back.

Technical Progress: Coupling mechanism: *oxygen decoordination*



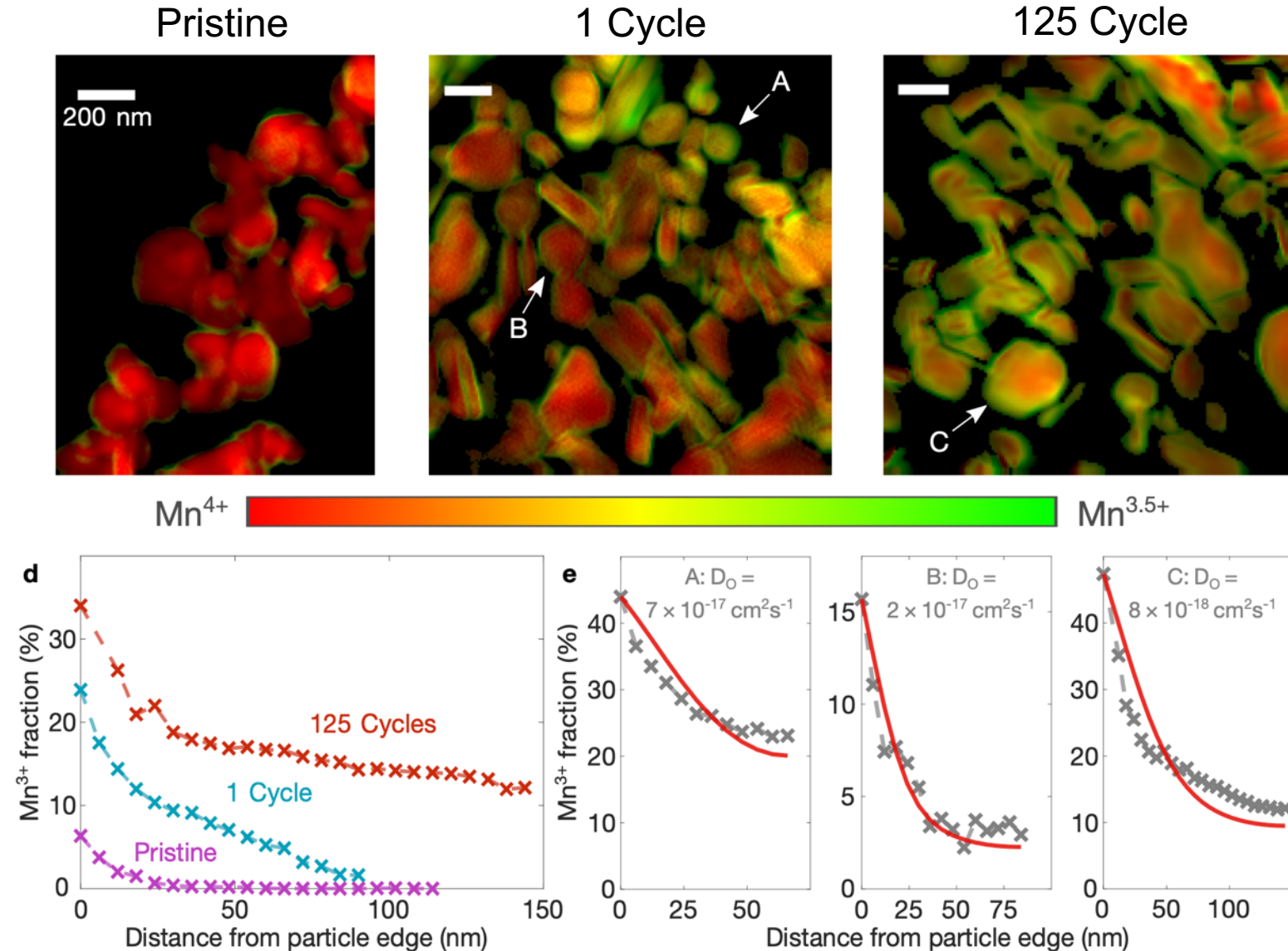
Upon TM migration, oxygen goes from being bonded to two TM to one TM, effectively generating a TM=O metal oxo species. This process stabilizes the oxygen against evolution and explains why oxygen oxidation and TM migration occur simultaneously.

Technical Progress: understanding long-term voltage fade



During cycling, LMR-NMC exhibits voltage fade even at low rate. This is accompanied by a gradual decrease in the Mn(4+) oxidation state in the discharge state as well as an increase in the transition metal disorder.

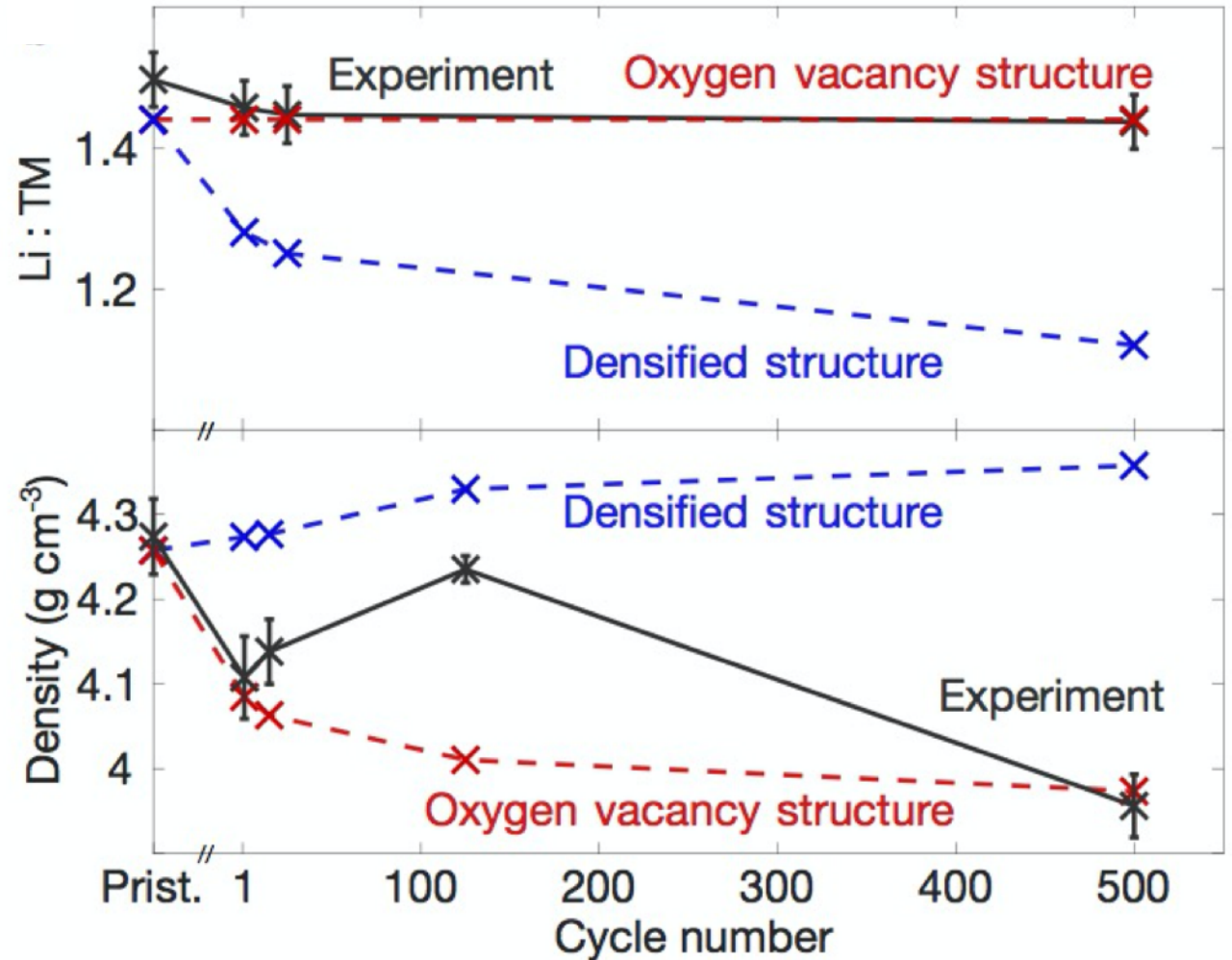
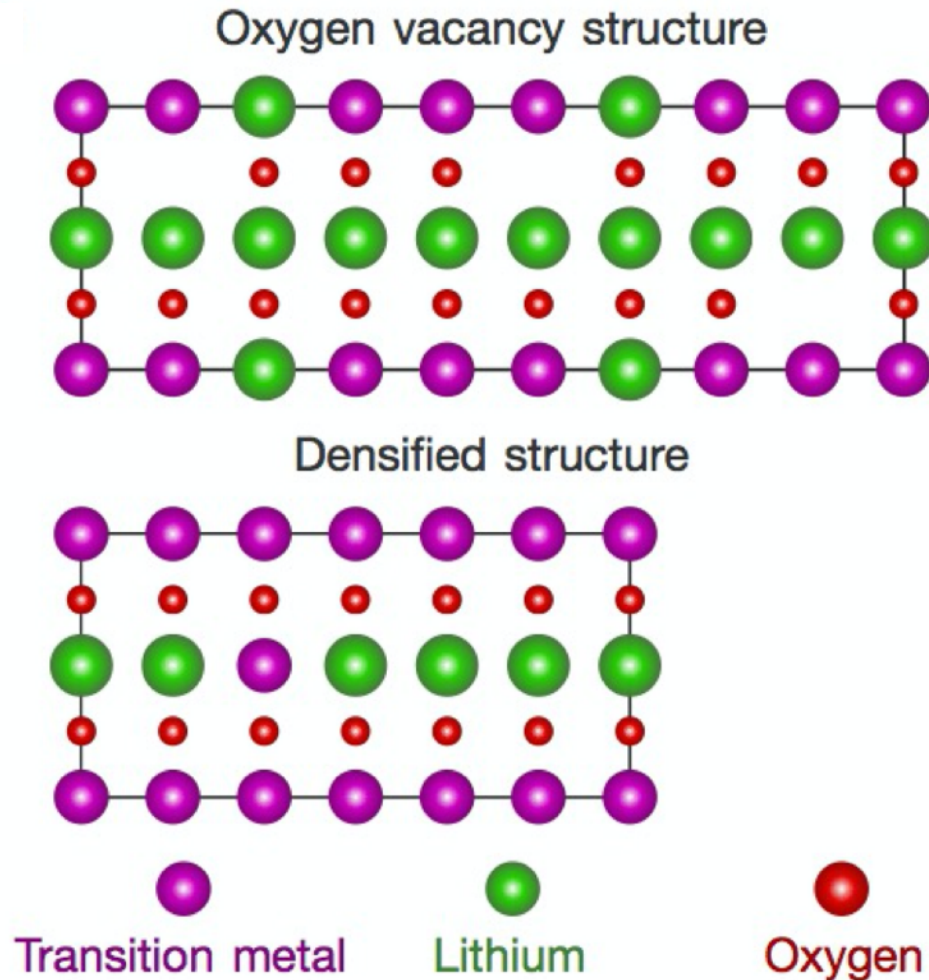
Technical Progress: oxygen diffuses with cycling



Eff. $D \sim 10^{-17} \text{ cm}^2 \text{ s}^{-1}$

With cycling, oxygen deficiency (as evidenced by Mn(3+) in the discharged state) first shows up at primary particle surface, then progresses inward to the particle, confirming that oxygen deficiency form deep in the bulk. 12

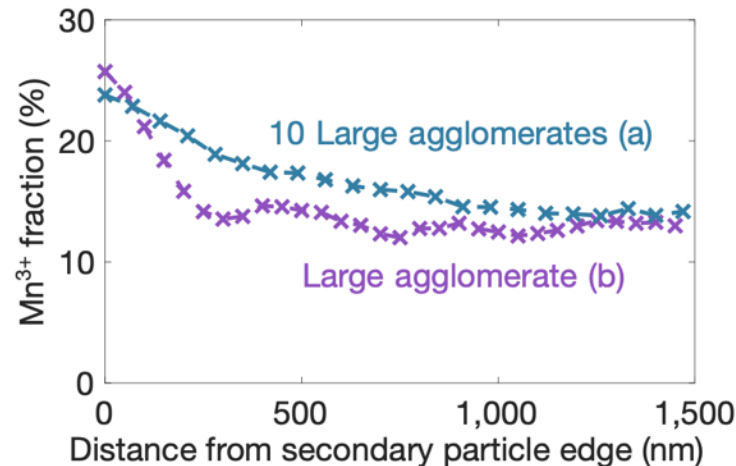
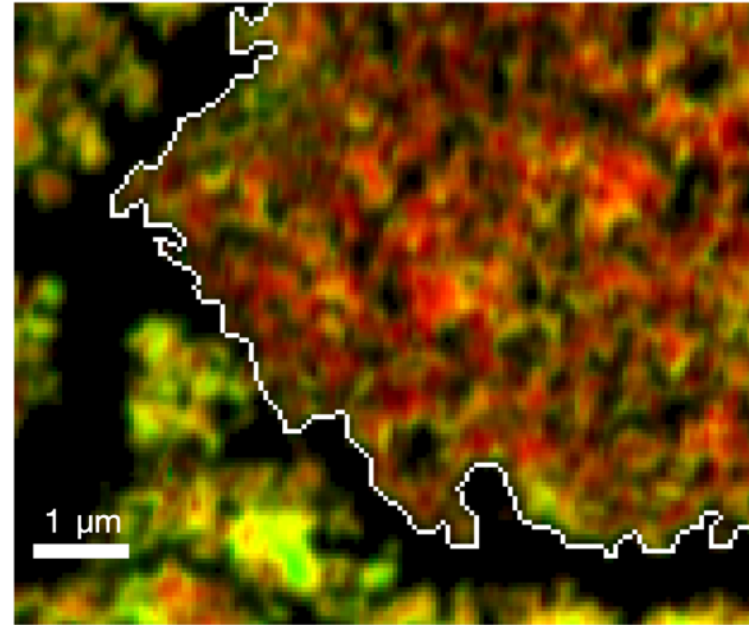
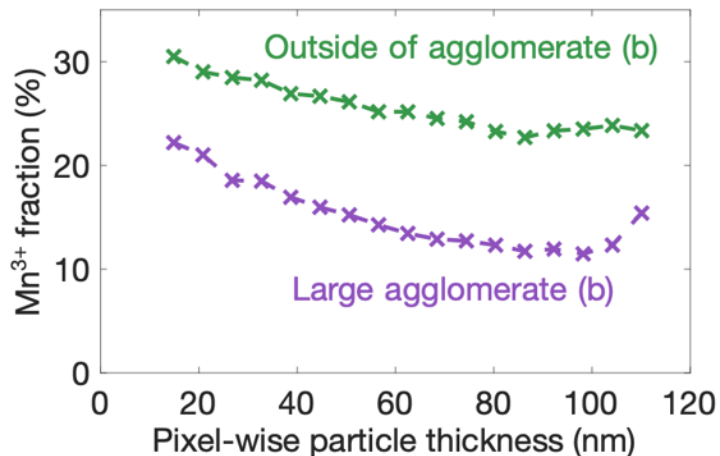
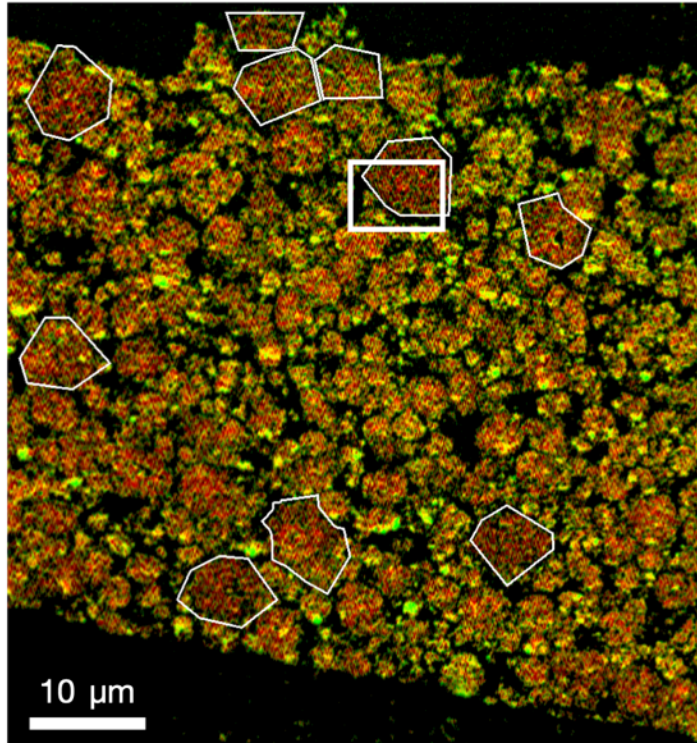
Technical Progress: confirming diffusing species as oxygen vacancies



Li to TM metal ratio and density distinguishes the two structure models: oxygen vacancies vs. densified. Experimental chemical analysis and pycnometry measurement suggest the presence of oxygen vacancies.

→ Oxygen vacancies explain why transition metal migration and voltage fade are coupled.

Technical Progress: secondary particle microstructure crucial



- Primary particles inside of the large agglomerate are significantly more oxidized, and thus release less oxygen, than those outside of the agglomerate. The implication therefore is that even primary particles of identical size and shape will exhibit a degree of oxygen release that is heavily dependent on their location within the secondary structure.
- We observe that within the large agglomerate, primary particles near the exterior are more reduced than those on the interior.
- Taken together, these findings reveal that primary particles originating from the interior of large secondary particles release comparably less oxygen.
- **This result advocates for morphological control as a potentially chemistry-agnostic method to achieve stability against oxygen release.**

Responses to Previous Year Reviewers' Comments

None

Collaboration and Coordination

Advanced Light Source, LBNL:

- Users facility accessed via proposal (no cost)
- Carry out X-ray microscopy experiments at beam line 11.0.2, 5.3.2
- Carry out resonant inelastic X-ray scattering at beam line 8.0.1

Molecular Foundry, LBNL:

- Users facility accessed via proposal (no cost)
- Carry out density functional theory simulations of lithium-excess layered oxides

Remaining Challenges and Barriers

None

Proposed Future Work

None

Summary

- Developed X-ray methods methods to quantify transition metal and oxygen redox partners at different SOC
- Employed X-ray diffraction to reveal local structure change in LMR-NMC which established how to prevent oxygen evolution at high voltage
- Developed X-ray microscopy to quantify nanoscale majority and minority redox partners spanning the length scales of lattice, interfaces, primary particles, agglomerates and electrodes.
- Proposed a decoordination model to explain why oxygen redox occurs simultaneously as metal migration
- Understood the mechanism of voltage fade in LMR-NMC, revealing the crucial role of oxygen vacancies